

# Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces

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Beamline: X11A

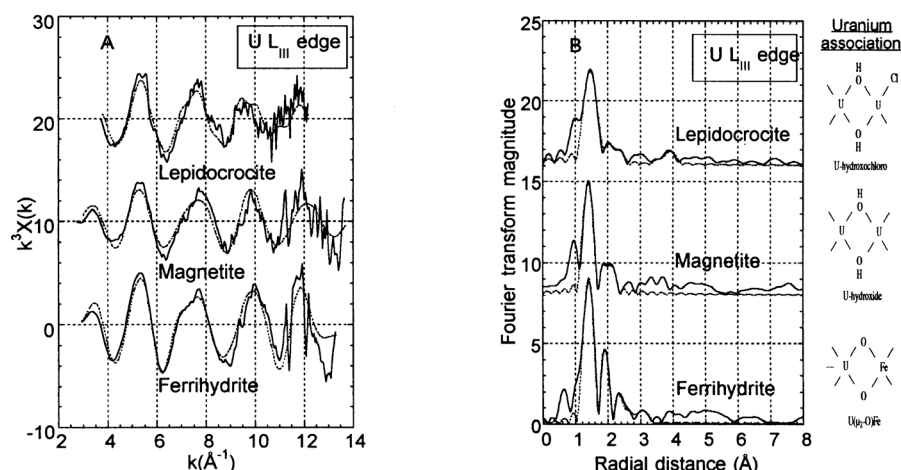
**Introduction:** This project addresses key fundamental issues involved in the use of simple and safe methods for the removal of radioactive contaminants from slightly contaminated steel and other surfaces at the DOE sites so that the metals can be reused. A specific goal of this research is to determine the nature of the association of radionuclides U, Co, Cs, and Sr with the metal surfaces commonly found at sites targeted for decontamination and decommissioning, such as stainless steel, plain carbon steel and copper.<sup>1-4</sup>

**Methods and Materials:** Oxides relevant to this study ferrihydrite, magnetite, and lepidocrocite were chosen after being identified on the surface of low carbon steel exposed to uranyl nitrate solution. Ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) was synthesized following precipitation of ferric nitrate at pH 7; magnetite ( $\text{Fe}_3\text{O}_4$ ) by oxidation of ferrous sulfate solution with  $\text{KNO}_3$  and  $\text{KOH}$ ; and lepidocrocite ( $\gamma\text{-FeOOH}$ ) by oxidation of  $\text{FeCl}_2$  at pH 8. Uranyl nitrate was coprecipitated with the iron at a stoichiometric ratio of 1:20. The association of uranium with the synthetically prepared iron oxides was determined by EXAFS at the  $\text{L}_{III}$  edge using fluorescence detection. The theoretical modeling code FEFF 7.02 was used to calculate the backscattering phase and amplitude information for individual neighboring atoms.

**Results:** Figure 1 shows the results of fitting of the raw  $k^3$ -weighted spectra (A) and Fourier-transformed data (B) for uranium incorporated into the oxide. The peaks in the Fourier transform represent coordination shells at radial distances from the uranium atom. A four shell fit (dotted line) was performed to duplicate the oscillations for ferrihydrite which included 2.0 axial O atoms at 1.79Å, a split in the equatorial shell consisting of 3.0 O atoms at 2.35Å and 2.0 O atoms at 2.54Å, and a U-Fe interaction at 3.42Å. The presence of two equatorial O atoms at 2.54Å is diagnostic for bidentate coordination of U to the Fe. A three shell fit duplicated the data for magnetite with 2.0 axial O atoms at 1.78Å, and a split in the equatorial O atoms with 1.9 O's at 2.35Å, and 1.8 O's at 2.43Å. The range of distances in the equatorial O atoms is typical for uranyl hydroxide formation. A four-shell fit for lepidocrocite sample included 2.0 axial O atoms, 3.1 equatorial O's at 2.33Å, a U-Cl interaction at 2.65Å, and a U-U interaction at 4.14Å. The presence of Cl was due to the addition of  $\text{FeCl}_2$  to the mixture during oxide formation.

**Conclusions:** The association of U in the oxide was dependent upon the initial conditions present during formation of the oxides. Uranium was chemically bound to the Fe in ferrihydrite as bidentate complex; magnetite as uranyl hydroxide form; and as U-hydroxochloro species with lepidocrocite.

**References:** <sup>1</sup>A.J. Francis, C.J. Dodge, Environ. Sci. Technol. **24**, 373 (1990); <sup>2</sup>T.D. Waite, J.A. Davis, T.E. Payne, G.A. Waychunas, Geochim. Cosmochim. Acta **58**, 5465 (1994); <sup>3</sup>P.R. Grossl, D.L. Sparks, Geoderma **67**, 87 (1995); <sup>4</sup>A.J. Francis, C.J. Dodge, Environ. Sci. Technol. **32**, 3993 (1998).



**Figure 1.** Uranium was associated with ferrihydrite as a bidentate complex with iron; as uranium hydroxide in magnetite; and uranium hydroxochloro species with lepidocrocite.